Link atom bond length effect in ONIOM excited state calculations

Marco Caricato, Thom Vreven, Gary W. Trucks, and Michael J. Frisch

Citation: The Journal of Chemical Physics **133**, 054104 (2010); doi: 10.1063/1.3474570
View online: http://dx.doi.org/10.1063/1.3474570
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/133/5?ver=pdfcov
Published by the AIP Publishing

Link atom bond length effect in ONIOM excited state calculations

Marco Caricato,[a] Thom Vreven, Gary W. Trucks, and Michael J. Frisch
Gaussian, Inc., 340 Quinnipiac St., Bldg. 40, Wallingford, Connecticut 06492, USA

(Received 23 February 2010; accepted 12 July 2010; published online 5 August 2010)

We investigate how the choice of the link atom bond length affects an electronic transition energy calculation with the so-called our own *N*-layer integrated molecular orbital molecular mechanics (ONIOM) hybrid method. This follows our previous paper [M. Caricato *et al.*, J. Chem. Phys. **131**, 134105 (2009)], where we showed that ONIOM is able to accurately approximate electronic transition energies computed at a high level of theory such as the equation of motion coupled cluster singles and doubles (EOM-CCSD) method. In this study we show that the same guidelines used in ONIOM ground state calculations can also be followed in excited state calculations, and that the link atom bond length has little effect on the ONIOM energy when a sensible model system is chosen. We also suggest further guidelines for excited state calculations which can help in checking the effectiveness of the definition of the model system and controlling the noise in the calculation. © *2010 American Institute of Physics*. [doi:10.1063/1.3474570]

I. INTRODUCTION

Hybrid methods are nowadays routinely and successfully used to investigate a variety of properties and reactions of large molecular systems especially of biological interest. They divide the system into regions, and treat with accurate and computationally expensive methods only the part where necessary, whereas the reminder is treated at a lower and less demanding level of theory. Most of these methods combine a quantum mechanical level with a molecular mechanical level, QM/MM,[1–3] and are applied to ground state problems. However, the study of excited state potential energy surfaces is becoming increasingly important in current research, especially in the biological and nanomaterial fields, and the availability of fast but accurate methods is very important.

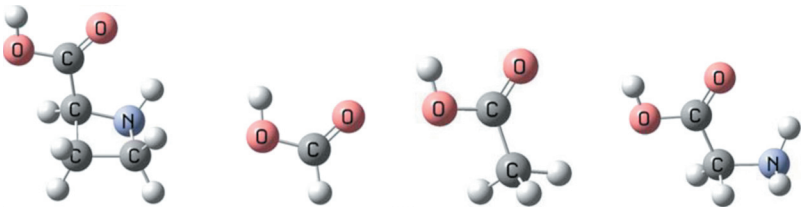
An alternative to traditional QM/MM approaches is the so-called our own N-layer integrated molecular orbital molecular mechanics method (ONIOM)[4–13] which, unlike the former methods that are formulated as summation, is formulated as extrapolation. ONIOM can combine more than two computational levels as well as the integration of two or more different quantum mechanical levels, QM/QM. Also, ONIOM can provide accurate treatment of electronic excited states since transition energies can be easily defined within the ONIOM scheme.[14] Although the behavior of ONIOM for ground state energies has been investigated in numerous works, there are only few reports in the literature on the calculation of transition energies of which several used QM/QM combinations (see Ref. 15 and references therein).

In a recent paper,[15] we presented promising results on the ability of ONIOM to accurately reproduce excitation energies obtained at a high and expensive level of theory like the equation of motion coupled cluster singles and doubles (EOM-CCSD)[16–24] while drastically reducing the computational effort. This can be achieved by defining a sensible high level region and treating the rest of the molecule at an appropriate lower level of theory such as configuration interaction singles (CIS), time-dependent Hartree–Fock (TDHF), or time-dependent density functional theory (TDDFT).

One of the most critical aspects of a hybrid method calculation is the partitioning of the system into layers. In ONIOM, covalent bonding between two regions leads to open valences in the model system that are saturated with link atoms (typically hydrogens). Other strategies can be followed to cap open valences in hybrid methods, for example, using effective potentials,[25,26] but the link atom is the simplest and most general, thus in line with the ONIOM approach. For ground state calculations, there are simple guidelines that should be followed in the definition of the model system,[13] for example, the cuts should be made on single, nonpolar, and nonconstrained bonds; an atom in the low level layer should not be bonded to two or more atoms in the high level layer.

A study by Derat *et al.*[27] showed that the exact value of the link atom bond length has a very small effect on the absolute ONIOM energy and an even smaller effect on optimized geometries. The aim of this work is thus to extend the investigations in Refs. 15 and 27 to whether the same definition of the link atom bond length can be retained for excited state calculations. This study makes use of the same test systems as in Ref. 15, since for these the influence of other factors on the ONIOM performance (partitioning, low level of theory, and basis set) has already been analyzed and this allows us to focus on the link atom. These systems include a variety of chemical groups and represent a significant spectrum of valence excitations. Excited states of a different nature, such as Rydberg or charge transfer, will be the subject of a sequent study. As in Ref. 15, we focus on the vertical excitation energy since this is the fundamental quantity that ONIOM must be able to reproduce in order to be useful in production calculations.

[a]Electronic mail: marco@gaussian.com.



(a)Real (b)Model 1 (c)Model 2 (d)Model 3

FIG. 1. Structures of the S-azetidine-2-carboxylic acid and the three model systems.

We stress that there are several issues in excited state calculations using hybrid methods which are not present for the ground state and for conventional methods. For example, the ordering of the states may not be the same between different levels of theory, and one must ensure to combine corresponding states. Therefore, a careful investigation of the strengths and weaknesses of such methods is extremely important before their wide application in production calculations. As illustrated in the following and summarized in Sec. IV, the results in this report and in Ref. 15 suggest that the same ONIOM ground state guidelines still hold, but we also add a more specific set for excited state calculations.

This paper is organized as follows. Section II reviews the theory of the ONIOM method and reports the computational details. Section III collects the results for the test cases we examined and discusses the aspects that influence the ONIOM final results. A summary of the discussions and general conclusions are reported in Sec. IV.

II. THEORY AND METHODS

The ONIOM energy for a two layer system with mechanical embedding is

$$E^{\mathrm{ONIOM}} = E^{\mathrm{high}}_{\mathrm{model}} + E^{\mathrm{low}}_{\mathrm{real}} - E^{\mathrm{low}}_{\mathrm{model}}, \tag{1}$$

where real and model refer to the full system and to the core region, respectively. The transition energy ΔE in the ONIOM scheme can be expressed as the difference of the ONIOM energies of the two states,

$$\begin{aligned}\Delta E^{\mathrm{ONIOM}} &= E^{*,\mathrm{ONIOM}} - E^{\mathrm{ONIOM}} \\ &= (E^{*,\mathrm{high}}_{\mathrm{model}} + E^{*,\mathrm{low}}_{\mathrm{real}} - E^{*,\mathrm{low}}_{\mathrm{model}}) \\ &\quad - (E^{\mathrm{high}}_{\mathrm{model}} + E^{\mathrm{low}}_{\mathrm{real}} - E^{\mathrm{low}}_{\mathrm{model}}) \\ &= (E^{*,\mathrm{high}}_{\mathrm{model}} - E^{\mathrm{high}}_{\mathrm{model}}) + (E^{*,\mathrm{low}}_{\mathrm{real}} - E^{\mathrm{low}}_{\mathrm{real}}) \\ &\quad - (E^{*,\mathrm{low}}_{\mathrm{model}} - E^{\mathrm{low}}_{\mathrm{model}}) \\ &= \Delta E^{\mathrm{high}}_{\mathrm{model}} + \Delta E^{\mathrm{low}}_{\mathrm{real}} - \Delta E^{\mathrm{low}}_{\mathrm{model}}. \end{aligned} \tag{2}$$

Only the model terms, at high and low level, depend on the nature and character of the link atom. The standard link atom is represented by a hydrogen atom and its bond length (r_{LA}) is obtained by scaling the original length of the atom that is substituted with a factor that depends on the typical bond distance of the atoms involved. In order to assess the effect of r_{LA} on $\Delta E^{\mathrm{ONIOM}}$, we investigated various bond lengths by varying the standard length in a range of ± 0.3 Å, with a step of 0.1 Å.

The same methods and basis sets of Ref. 15 are used. The level of theory that we want to approximate with ONIOM (the *target*) is EOM-CCSD with the 6-311 +G(d,p) basis set. This is also used as high level in the ONIOM calculations. For the first compound, we test various low levels: EOM-CCSD (with a smaller basis set than the target), CIS, TDHF, and TDDFT with the B3LYP hybrid functional;[28–30] for the others we only test TDDFT, as this provided, on average, the best performance in Ref. 15. Additionally, two basis sets at low level are considered for the first molecule, 6-311+G(d,p) and 6-31+G(d), denoted L and M, respectively, as in Ref. 15; for the other molecules only the L basis set is used. All the calculations were performed with the GAUSSIAN 09 suite of programs.[31]

The dependence of the ONIOM transition energy from r_{LA} is reported as the error with respect to the target,

$$\mathrm{Error}(\Delta E, r_{\mathrm{LA}}) = \Delta E^{\mathrm{target}} - \Delta E^{\mathrm{ONIOM}}(r_{\mathrm{LA}}). \tag{3}$$

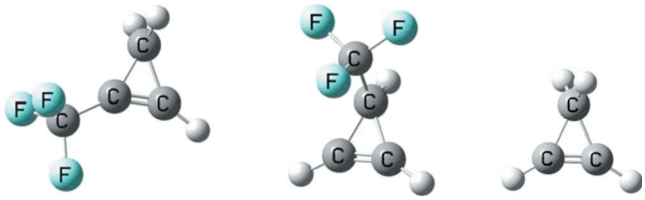
In this way the effect of the link atom can be directly compared to the overall ONIOM error on this property.

Ground (E_{GS}) and excited (E_{exc}) state absolute energies are reported as well as $\Delta E^{\mathrm{high}}_{\mathrm{model}}$ and $\Delta E^{\mathrm{low}}_{\mathrm{model}}$. However, since comparing ONIOM absolute energies with different combinations of levels of theory is as meaningless as comparing the absolute energies of two different conventional methods, the results are reported as the variation of E_{GS}, E_{exc}, $\Delta E^{\mathrm{high}}_{\mathrm{model}}$, and $\Delta E^{\mathrm{low}}_{\mathrm{model}}$ varying r_{LA} from its standard value. The x axis in the plots only indicates the r_{LA} shift (Å) from the standard value (reported in the text).[32] The trends of the energy shifts allow to assess how the different parts of the ONIOM energy depend on r_{LA}, and if and how $\Delta E^{\mathrm{ONIOM}}$ is influenced by cancellation of errors.

III. RESULTS AND DISCUSSION

In this work, four compounds from our previous work on transition energy calculations with ONIOM (Ref. 15) are considered. This choice allows us to investigate various kinds of chemical groups for a series of excitations where the effect of other ONIOM parameters, such as the choice of the model system, the low level of theory, and the basis set, is already known. The geometries are thus the same as in Ref. 15.

The first system, the S-azetidine-2-carboxylic acid, shown in Fig. 1(a), is studied in detail to examine how the choice of r_{LA} affects $\Delta E^{\mathrm{ONIOM}}$ in combination with the other parameters mentioned above. Three model systems are tried as defined in Ref. 15 and shown in Figs. 1(b)–1(d). Among these models, only partition 1 follows the ONIOM guidelines defined in Ref. 13. Models 2 and 3, on the other hand, cut the four-member ring and the C–N bond corresponding to constrained and polar bonds, respectively. Although this drastic partitioning is not recommended in production calculations,



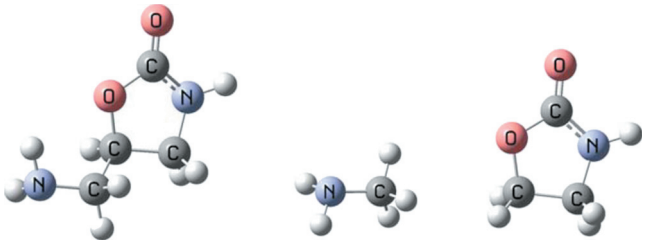
(a)Real, A (b)Real, B (c)Model

FIG. 2. Structures of (a) 1-trifluoro-methyl-cyclopropene, (b) 3-trifluoro-methyl-cyclopropene, and the model system.

it allows for a stringent test of the effect of the link atom and can provide information that can be useful in general cases.

For the remaining molecules, we selected only the model systems that follow the guidelines,[13] and the low level method and basis set that provided on average the best performance in Ref. 15: TDDFT/L. The second system includes two substituted cyclopropenes, where the CF_3 group is bonded to two different centers on the central structure, see Figs. 2(a) and 2(b), for which we consider the first two transitions. In this case, the same model system can be defined, although the link atom is bonded to different carbon centers. Thus, we can simultaneously analyze the r_{LA} effect on two excitations and two positions. Also for the last system, R-5-aminomethyl-2-oxazolidinone, shown in Fig. 3(a), we study the first two transitions. However, those are mainly localized around two different molecular groups, and each requires the definition of a different model system with the cuts involving the same C–C bond.

Before moving to the detailed analysis of the new data, let us briefly summarize the ONIOM performance on these molecules from our previous work. For the carboxylic acid (Table III in Ref. 15), ΔE^{target} (conventional EOM-CCSD/L on the entire system) is 5.93 eV. The best compromise between accuracy and computational effort was obtained with ONIOM using model 1 in combination with TDDFT/L as low level, which yields an error of −0.02 eV with a calculation speed-up of 29 times. CIS and TDHF as low level with this model yield absolute errors larger than 0.1 eV. Models 2 and 3 provide small absolute errors with all the methods, 0.01–0.07 eV, but the calculation speed-up is smaller, 7 and 3 times, respectively. EOM-CCSD/M as low level in ONIOM provides very small errors with all the models, 0.002–0.02 eV, but the $\Delta E^{\text{low}}_{\text{real}}$ term becomes the bottleneck step of the calculation with only a 2.5 speed-up. ONIOM always improves the results over the conventional calculations ($\Delta E^{\text{high}}_{\text{model}}$ and $\Delta E^{\text{low}}_{\text{real}}$) with all the methods and all the models. Although models 2 and 3 do not follow the standard ONIOM partitioning guidelines this does not lead to a poor performance in this case. For the cyclopropenes (Tables VI and VII in Ref. 15), the target transition energies are 6.88 and 7.09 eV for the CF_3 group in position one and 7.17 and 7.48 eV for CF_3 in position three. The errors for the $\Delta E^{\text{high}}_{\text{model}}$ term are small in the first case (−0.03 and −0.004 eV) but rather large in the other (0.32 and 0.44 eV), whereas the ΔE^{ONIOM} errors are always below 0.1 eV. This indicates that ONIOM is able to provide a balanced description of this property independent of the strength of the substituent effect. For R-5-aminomethyl-2-oxazolidinone, the target values are 6.32 and 6.71 eV and the $\Delta E^{\text{high}}_{\text{model}}$ errors are 0.40 and 0.03 eV, respectively, whereas the corresponding ΔE^{ONIOM} errors are 0.04 and −0.02 eV, which reflects the ONIOM ability to capture the substituent effect when necessary.



(a)Real (b)Model 1 (c)Model 2

FIG. 3. Structures of R-5-aminomethyl-2-oxazolidinone and the two model systems. Model 1 is used to study the first electronic transition, model 2 the second transition.

A. S-azetidine-2-carboxylic acid model 1

As pointed out in Sec. III, model 1 shown in Fig. 1(b) is defined following the ONIOM partitioning guidelines. The standard r_{LA} in this case is 1.097 Å (the original C–C length is 1.515 Å). The absolute ground and excited state energies, the ΔE^{ONIOM} error, and the ΔE_{model} as a function of the LA length are reported in Figs. 4–6.

The effect of varying r_{LA} is similar for ground and excited electronic state energies for all the methods. The overall effect is much smaller with CCSD and DFT as low levels than for HF probably because the latter lacks correlation effects. At negative shifts, the effect for CCSD is quite large, but this is mainly due to the basis set. This is evident when comparing the curves for DFT/L and M and for HF/L and M. In the range of ±0.1 Å, the curves are basically flat for CCSD and DFT in the low level in the ground state, while they have an opposite, although small, slope in the excited state. In the same range, HF has a variation of ±0.05 eV for both ground and excited states (CIS and TDHF).

Figure 5 shows that the variation of ΔE^{ONIOM} with r_{LA} is small (<0.1 eV) for all the methods over the whole shift range since this is an energy difference and the trends for the absolute energies are similar. The variation is small with CIS/L and TDHF/L even for large Δr_{LA}. It is larger for EOM-CCSD/M and for TDDFT/L, varying about 0.1 eV between the two extremes for the latter method. The effect on EOM-CCSD/M is again mainly due to the basis set. This is confirmed when considering the difference between the CIS/L and M curves (or TDHF/L and M) compared to the EOM-CCSD/L and M curves. Therefore, when the effect of the method is small, as for the HF based methods, the effect of the basis set might be more significant. For TDDFT the sensitivity of the method to r_{LA} is larger than with the other methods, but in the opposite direction to the basis set.

Figure 6 shows the dependence on r_{LA} of ΔE_{model}. For all the wave function methods, ΔE_{model} varies very little with r_{LA}, especially in the ±0.1 Å region and the variation is very similar among them. DFT shows the largest dependence and thus it differs more from the high level method (EOM/L).

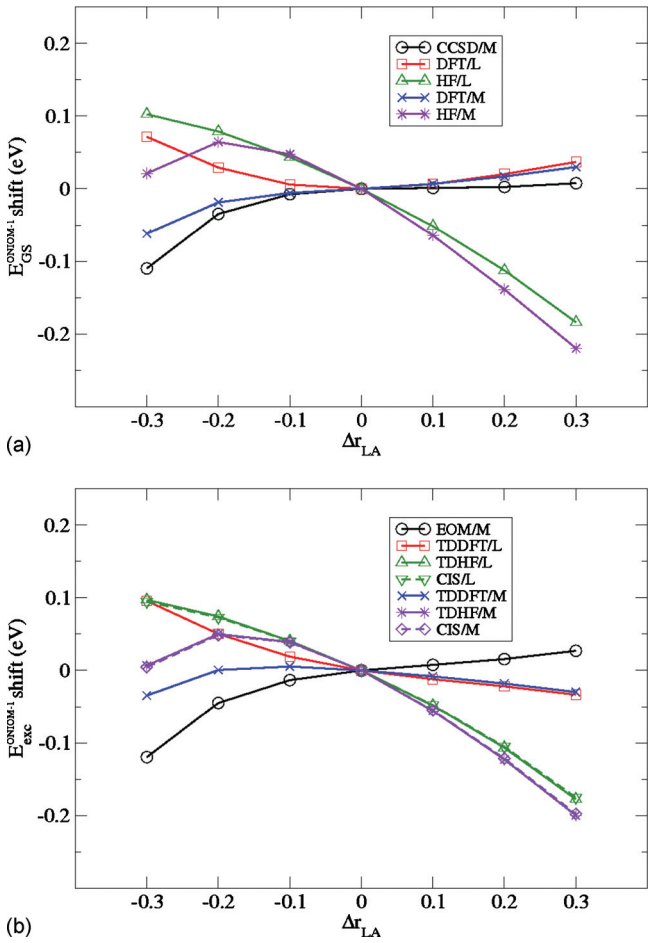


FIG. 4. Carboxylic acid ONIOM-1 ground (a) and excited state (b) energy shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}.

These trends illustrate that the dependence of ΔE^{ONIOM} on r_{LA} is not only small because of the cancellation between the high and low level model calculations, but also because of the small dependence of the individual transition energies.

When we compare the ΔE^{ONIOM} dependence on r_{LA} with the total ONIOM error, TDDFT as low level is always closer to the target than CIS and TDHF especially for

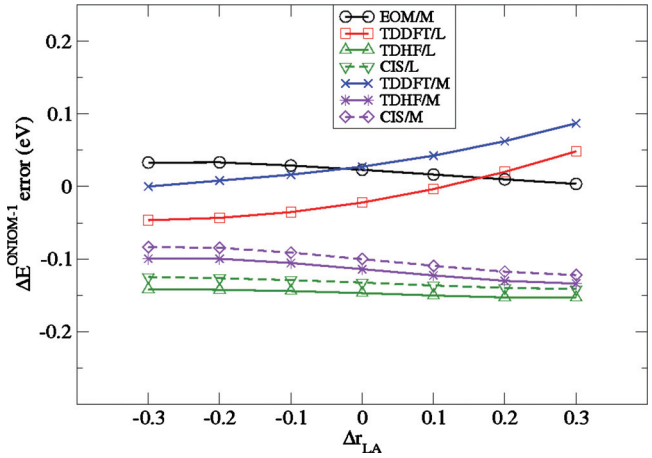


FIG. 5. Carboxylic acid ONIOM-1 transition energy error (eV), Eq. (3), as a function of the r_{LA} shift (Å) from the standard value (see text).

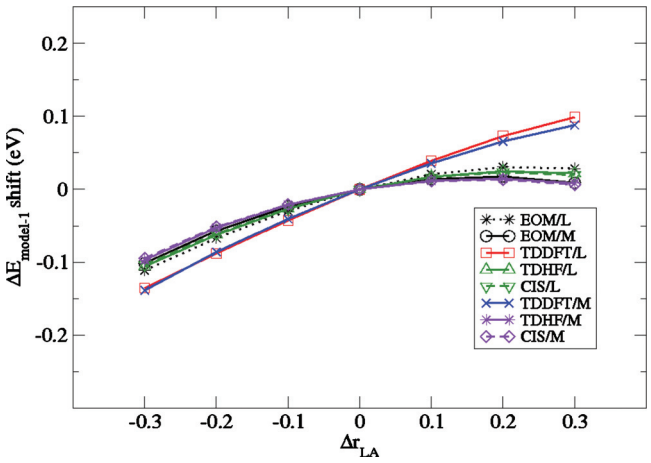


FIG. 6. Carboxylic acid $\Delta E_{model-1}$ shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text). EOM/L is the high level, whereas the rest are the low levels. The reference value for each method is the energy with the standard r_{LA}.

$-0.1 \leq \Delta r_{LA} \leq 0.1$ Å which define a sensible range of lengths. This shows that the link atom effect on the ONIOM final performance is considerably less important than the choice of the method and basis set for the low level. In the same range of shifts and with TDDFT and EOM-CCSD in the low level, the link atom effect is small on the transition energy as well as on the absolute energies. This shows that the small ΔE^{ONIOM} dependence is not the result of cancellation of errors between the ground and the excited state energies, and the definition of the link atom bond length for the ground state is appropriate for the excited state.

B. S-azetidine-2-carboxylic acid model 2

Model 2 is a more complicated case since it involves the substitution of two atoms. Additionally, the cuts involve the four-member ring (constrained bonds) and a nitrogen (polar bond). This model is built in a way not usually recommended for ONIOM. The original C–C and C–N bond lengths are 1.561 and 1.471 Å, respectively. The standard r_{LA} are 1.130 and 1.157 Å, respectively. Note that the LA bond for the carbon is longer than in model 1 because the original C–C bond is longer. The third C–H bond length is 1.094 Å showing that the LA bonds are slightly elongated. We carry out the analysis of the two link atoms separately, so the shift of one link atom is considered while the other one is fixed at its standard length. Figures 7–12 report the absolute energies, the ΔE^{ONIOM} errors, and ΔE_{model} as a function of Δr_{LA} for C–H(N) and for C–H(C), respectively. In this section only the largest basis set is considered for each low level method to simplify the discussion.

Figure 7 shows trends similar to the previous case for E_{GS}^{ONIOM} and E_{exc}^{ONIOM} despite a C–N bond is cut instead of a C–C bond. The r_{LA} effect is large for HF, CIS, and TDHF as low levels over the entire range of shifts (>0.2 eV). The curves for DFT and CCSD are considerably flatter for both states especially in the region of ±0.1 Å. Similar trends for the absolute energies means very small effect for the transition energy with all the methods (see Fig. 8). Figure 9 shows

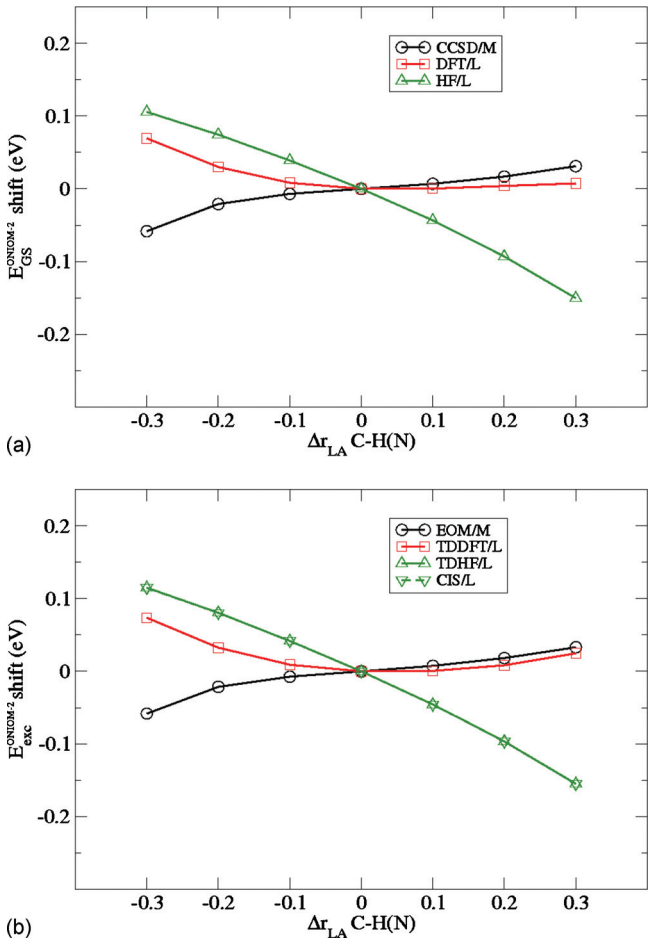


FIG. 7. Carboxylic acid ONIOM-2 ground (a) and excited state (b) energy shift (eV) as a function of the C–H(N) r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}.

that the small dependence of ΔE^{ONIOM} on r_{LA} is not only due to cancellation of errors as ΔE^{high}_{model} and all ΔE^{low}_{model} vary little with r_{LA}.

As in the previous choice of partitioning, the effect of the link atom on ΔE^{ONIOM} is negligible compared to the choice of the low level method. Although CIS and TDHF

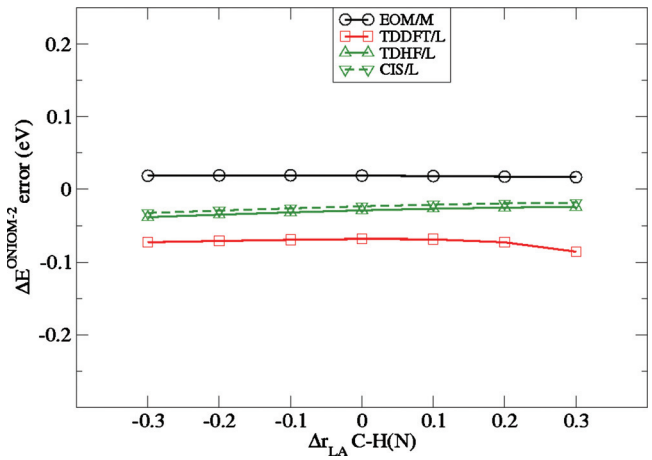


FIG. 8. Carboxylic acid ONIOM-2 transition energy error (eV), Eq. (3), as a function of the C–H(N) r_{LA} shift (Å) from the standard value (see text).

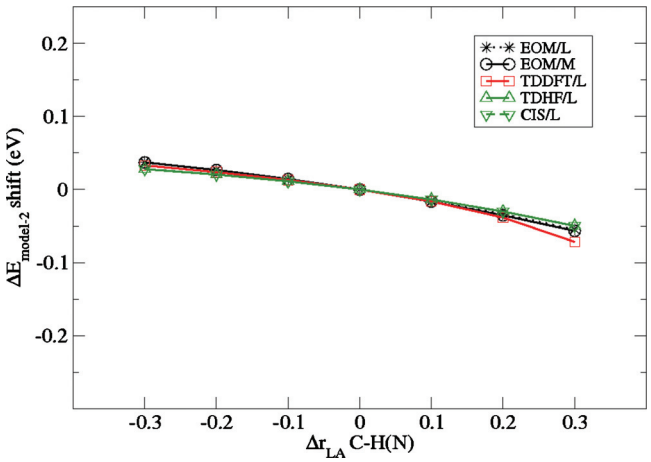


FIG. 9. Carboxylic acid $\Delta E_{model-2}$ shift (eV) as a function of the C–H(N) r_{LA} shift (Å) from the standard value (see text). EOM/L is the high level, whereas the rest are the low levels. The reference value for each method is the energy with the standard r_{LA}.

present smaller errors in ΔE^{ONIOM} than TDDFT, for the latter varying r_{LA} in the range of ± 0.1 Å produces a small effect on both the absolute and the transition energies.

In contrast, Fig. 10 shows a large dependence of DFT on the C–H(C) r_{LA} for the excited state, whereas this effect is

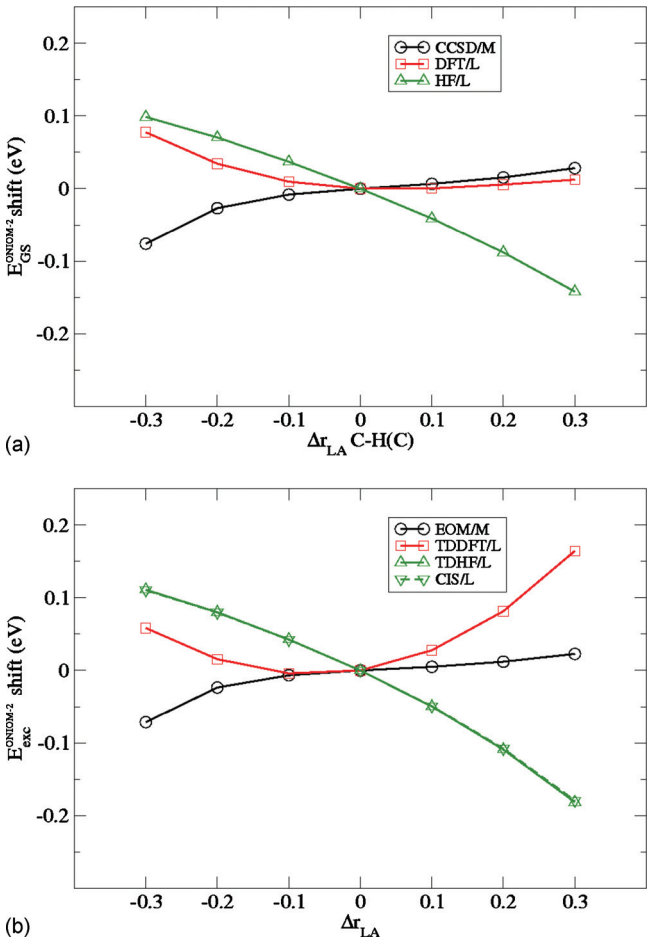


FIG. 10. Carboxylic acid ONIOM-2 ground (a) and excited state (b) energy shift (eV) as a function of the C–H(C) r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}.

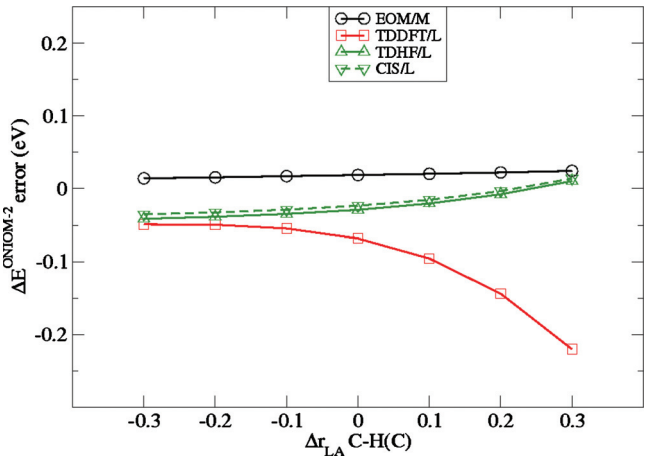


FIG. 11. Carboxylic acid ONIOM-2 transition energy error (eV), Eq. (3), as a function of the C–H(C) r_{LA} shift (Å) from the standard value (see text).

small and comparable to the C–H(N) link atom for the ground state. Such dependence is consequently reflected in the transition energy, as shown in Fig. 11. In contrast, the behavior of EOM-CCSD, CIS, and TDHF is similar to the previous cases. Figure 12 shows a small variation of ΔE_{model} for the wave function methods in the region between ± 0.1 Å, whereas it varies more at larger Δr_{LA}. This implies that the small variation of ΔE^{ONIOM} for these methods at longer lengths is due to cancellation of error between the high and low levels.

For a further investigation of such effect on TDDFT the $\Delta\Delta E_{model}=\Delta E^{high}_{model}-\Delta E^{low}_{model}$ by varying both r_{LA} is reported in Fig. 13. Figure 13 clearly shows that the effect of the C–H(C) length is larger than that of C–H(N). It also shows that smaller differences are shown at shorter lengths.

This behavior can be explained by a simple analysis of the DFT natural transition orbitals (NTOs)[33] involved in this transition. Figure 14 reports the occupied and virtual NTOs for the real and the model systems. These orbitals represent more than 99% of the transition confirming that this is a one-electron excitation. From Fig. 14, it is evident that the H link atom that replaces N is not involved directly in the transition because it lays on the nodal plan of the −COOH group. Thus, its bond length is not a crucial factor (despite a polar bond being cut). On the other hand, the C–H(C) link atom is out of plane and has a more direct role in the transition, thus its bond length is more relevant. The longer the bond, the more distorted the electronic density, and this is described very differently by EOM-CCSD (or other HF based methods) and DFT. In fact, the relative contribution of other orbitals becomes more important when elongating the bond, and the descriptions of this transition by methods of different origins diverge. However, the standard r_{LA} is in a range where this discrepancy is still small.

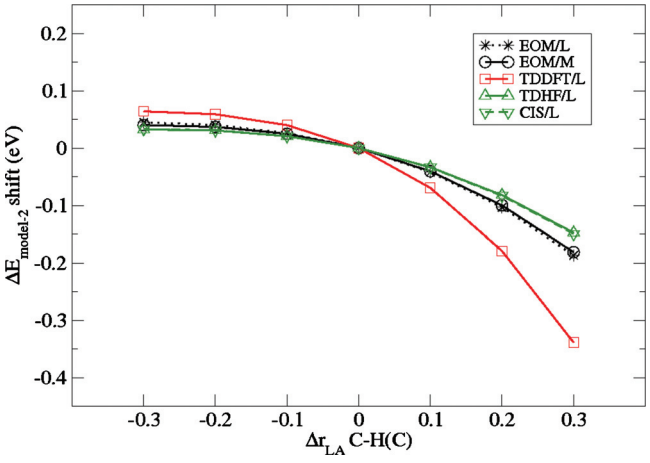


FIG. 12. Carboxylic acid $\Delta E_{model-2}$ shift (eV) as a function of the C–H(C) r_{LA} shift (Å) from the standard value (see text). EOM/L is the high level, whereas the rest are the low levels. The reference value for each method is the energy with the standard r_{LA}.

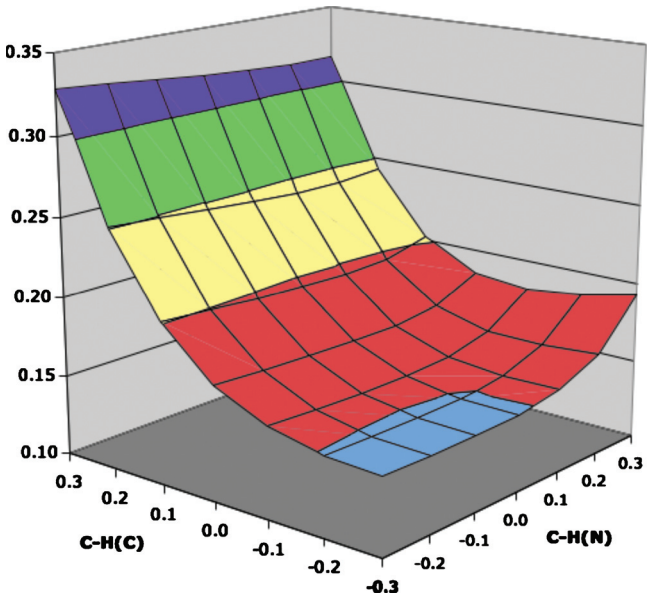


FIG. 13. Carboxylic acid $\Delta\Delta E_{model}$ (eV) as a function of both the C–H(N) and the C–H(C) r_{LA} shifts (Å) from the standard values (see text) for ONIOM-2 with TDDFT in the low level.

Although this model provides a behavior similar to model 1 for the ground state, it shows that the description of

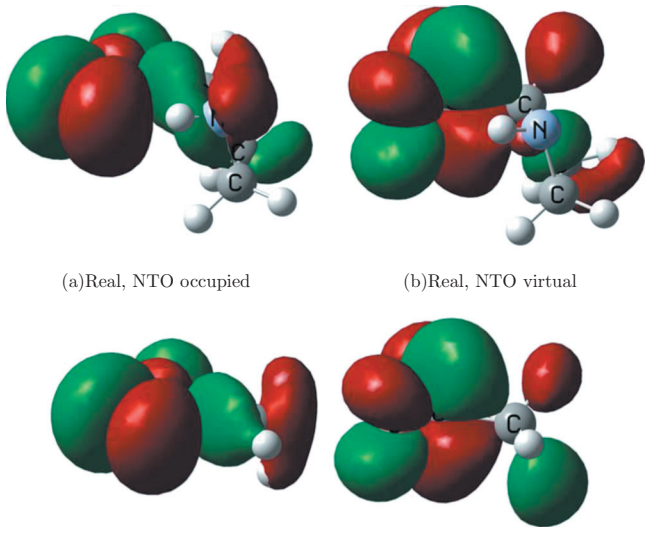


FIG. 14. Carboxylic acid natural transition orbitals involved in the electronic transition for the real and the model 2 systems with TDDFT.

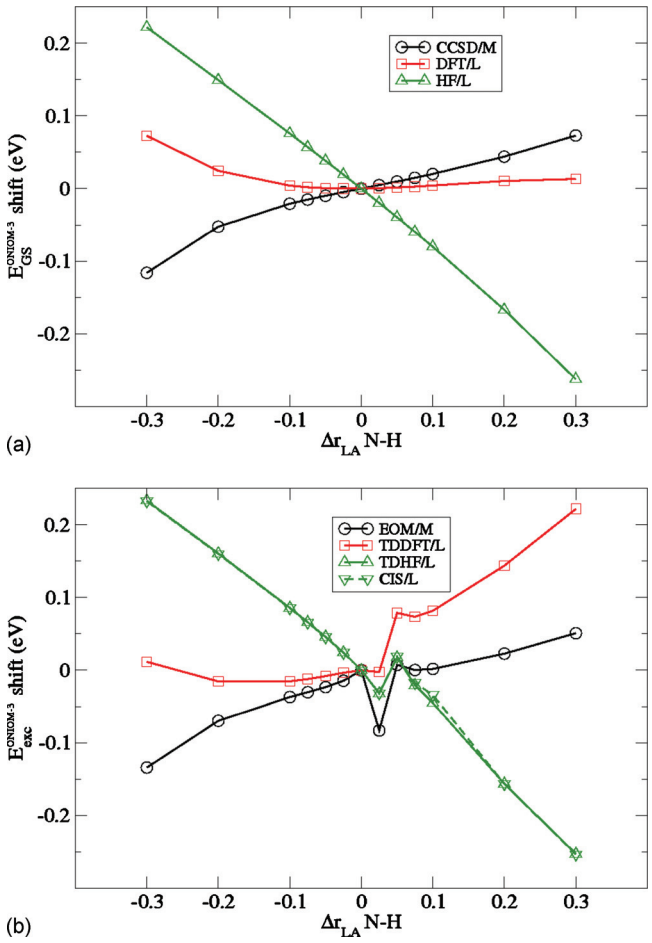


FIG. 15. Carboxylic acid ONIOM-3 ground (a) and excited state (b) energy shift (eV) as a function of the N–H r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}. In the region between −0.1 and 0.1 Å more points are considered with a step of 0.025 Å.

an excited state is more delicate. Therefore, the choice of the model system, which in this case did not follow the ONIOM guidelines, is more critical for the excited state calculation.

C. S-azetidine-2-carboxylic acid model 3

Model 3 also has two link atoms. The one that replaces the C is the same as in model 2, and the other one replaces the C bonded to the N; therefore, this model is not defined in the recommended manner. In this section only the effect of the latter r_{LA} is analyzed. The original N–C bond length is 1.488 Å, whereas the corresponding standard r_{LA} is 1.042 Å. The other N–H bond length is 1.016 Å.

The absolute energies and the ΔE^{ONIOM} errors are reported in Figs. 15 and 16. Although the ground state dependence is similar to what we have found with the other models, the excited state and the transition energies show an irregular behavior between 0 and 0.1 Å for all the methods. In order to obtain a more detailed description of this area, a smaller step, 0.025 Å, is used between −0.1 and 0.1 Å.

Understanding the reason of such irregular behavior requires the analysis of the ground and the transition energies for the model only with the high and all the low level methods. The dependence of these quantities on the link atom

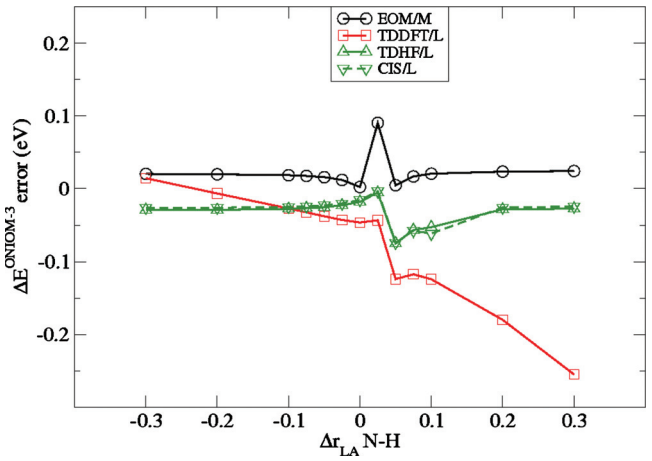


FIG. 16. Carboxylic acid ONIOM-3 transition energy error (eV) as a function of the N–H r_{LA} shift (Å) from the standard value (see text). In the region between −0.1 and 0.1 Å more points are considered with a step of 0.025 Å.

bond length is reported in Fig. 17. Figure 17(a) shows that the curves for the ground state are similar for all the methods in the high and low levels. The energy profiles are smooth; therefore, the ONIOM ground state energies with all the low

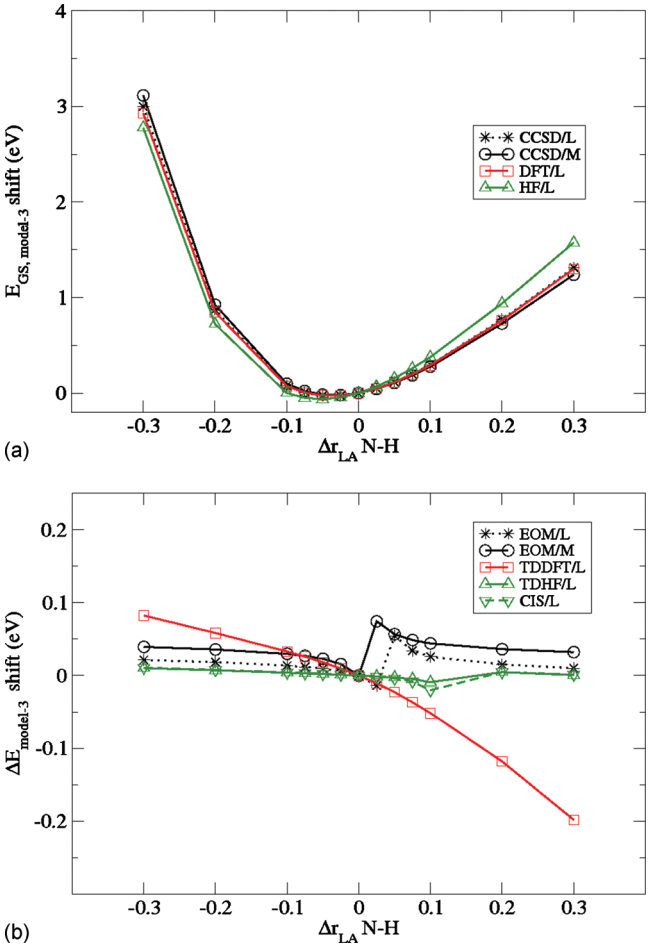


FIG. 17. Carboxylic acid model 3 ground state (a) and transition (b) energy shift (eV) as a function of the N–H r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}. In the region between −0.1 and 0.1 Å more points are considered with a step of 0.025 Å.

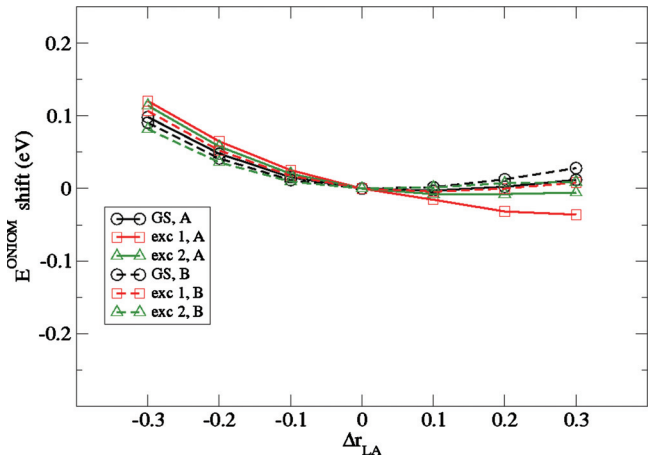


FIG. 18. Substituted cyclopropene ONIOM ground and excited state energy shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}.

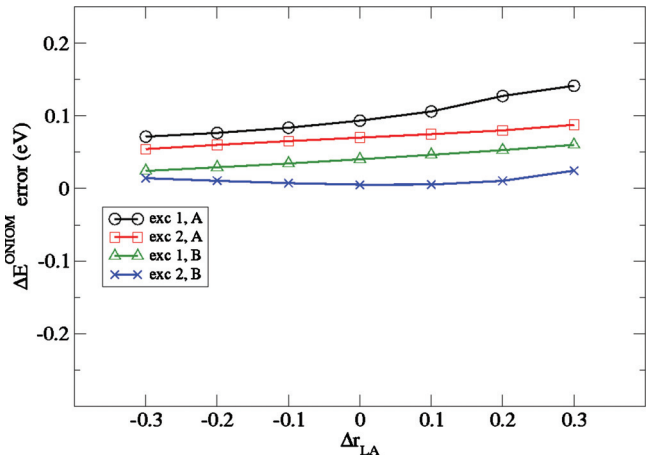


FIG. 19. Substituted cyclopropene ONIOM transition energy error (eV), Eq. (3), as a function of the r_{LA} shift (Å) from the standard value (see text).

level methods yield the trends observed for the other models. On the other hand, the individual ΔE_{model} [reported in Fig. 17(b)] show an irregular change in the region of 0–0.1 Å for EOM-CCSD with both basis sets.

This can be explained by this link atom interaction with the electronic distribution around the other link atom, which participates to the electronic transition of the model system, as showed in Sec. III B. This interaction provokes a change in the order of the excited states for the high level method. Between 0.025 and 0.050 Å for EOM-CCSD/L, the mixing of the two states that are crossing leads to the irregular change in the transition energy of the state that we are considering. The same pattern is shown by EOM-CCSD/M but at a shorter length [see Fig. 17(b)]. The CIS and TDHF wave functions do not have the flexibility to mix the states even though the inversion of the order of the excited states occurs. Thus, the CIS and TDHF curves in Fig. 17 are quite flat. TDDFT exhibits no inversion in the order of the states, although there is a partial mixing between them along the whole range of Δr_{LA} considered that is responsible for the shape of the curve in Fig. 17(b).

Since the ONIOM formula in Eq. (2) includes the difference between the energies of the model system with the high and low level methods, the ONIOM total excited state and transition energies in Figs. 15(b) and 16 yield such irregular behavior in the region of mixing of the excited states. For the transition energy and the HF based methods in the low level, the r_{LA} effect is negligible outside this region (at shifts smaller than 0 and larger than 0.1 Å), and the character of the state is well determined. This is not the case for TDDFT where the mixing of the states continues over the entire range of bond lengths.

This example reports a case where the E_{exc}^{ONIOM} dependence on r_{LA} is far larger than for E_{GS}^{ONIOM}. Although the standard value of r_{LA} is outside the problematic region with small errors in the transition energies, the use of this model (defined outside the usual ONIOM guidelines) for other properties, for example, geometry optimizations, may not be reliable if the N–C bond in the real system (and therefore the corresponding link atom bond) would become longer.

D. Substituted cyclopropenes

These two molecules represent an interesting case because the same model system, Fig. 2(c), can be defined for both (although the geometries of the model systems are different as they depend on different real systems). Thus, the effect of the link atom can be studied on two different positions. For simplicity, we will refer to 1-trifluoro-methyl-cyclopropene as system "A" and to 3-trifluoro-methyl-cyclopropene as system "B." The first two electronic transitions, $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively, are studied for both molecules. For A, r_{LA}=1.067 Å, whereas for B, r_{LA}=1.092 Å. The original C–C bond lengths are 1.473 and 1.508 Å, respectively. Additionally, for A, the C–H bond length on the other carbon center involved in the double C=C bond is 1.076 Å. For B, the other C–H bond on the same carbon center connected to the link atom is 1.090 Å.

Figure 18 shows that the total ONIOM energy varies very little with r_{LA} for both molecules. Therefore, the change is similar between the ground and the excited states for the states considered. This corresponds to very small changes for

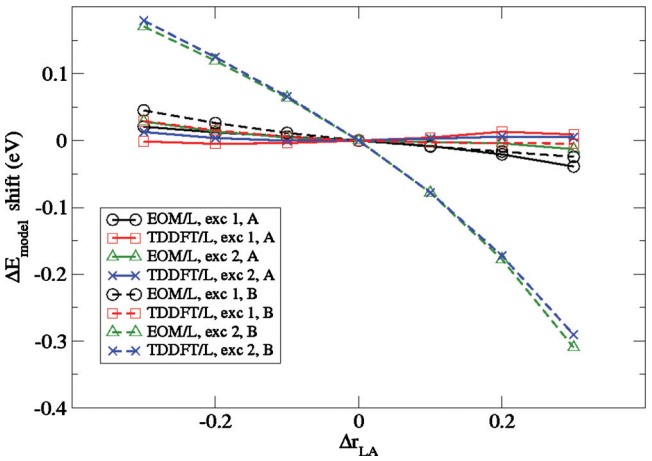


FIG. 20. Substituted cyclopropene model system transition energy shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text).

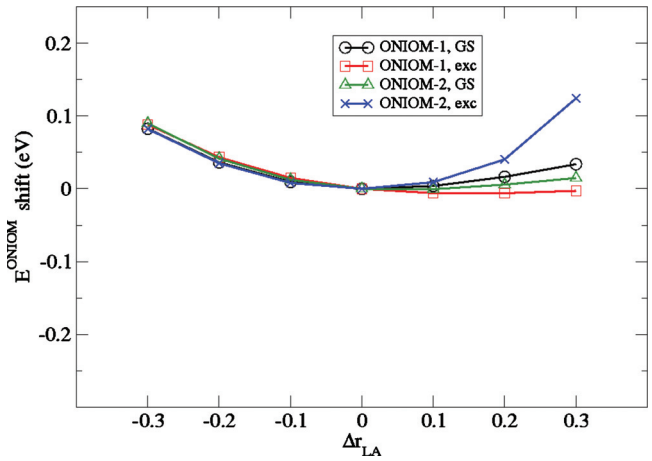


FIG. 21. R-5-aminomethyl-2-oxazolidinone ONIOM ground and excited state energy shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text). The reference value for each method is the energy with the standard r_{LA}.

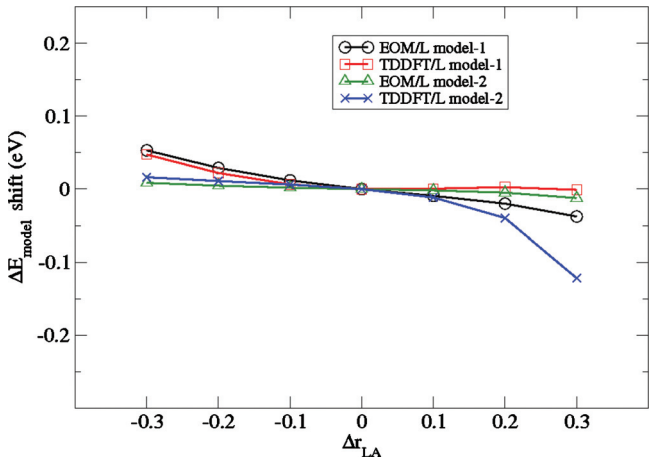


FIG. 23. R-5-aminomethyl-2-oxazolidinone model system transition energy shift (eV) as a function of the r_{LA} shift (Å) from the standard value (see text).

ΔE^{ONIOM} (see Fig. 19) especially in the range of $-0.1 \leq \Delta r_{LA} \leq 0.1$ Å. Figure 19 also outlines that, within such range, the link atom effect is considerably smaller than the total ONIOM error, as defined in Eq. (3). Additionally, Fig. 20 clarifies that, in most cases, the small link atom effect is not just a cancellation of errors between the high and the low levels since the transition energies of the model systems do not strongly depend on it. The only exception is the second transition for system B. The reason is that the link atom is in a region involved in the transition (see the NTOs in the supporting material). In contrast to the case in Sec. III B, the variation is basically the same for the high and low levels of theory; therefore, the overall *effect* on ONIOM is negligible. This is expected since the model in Sec. III B violates the ONIOM guidelines while the model in this section follows them.

Despite the good ONIOM performance in approximating the target calculations for both these systems, attention must be paid to the combination of the terms in Eq. (2) as the order of the transitions for TDDFT is inverted with respect to EOM-CCSD. Nevertheless, this test case seems to confirm

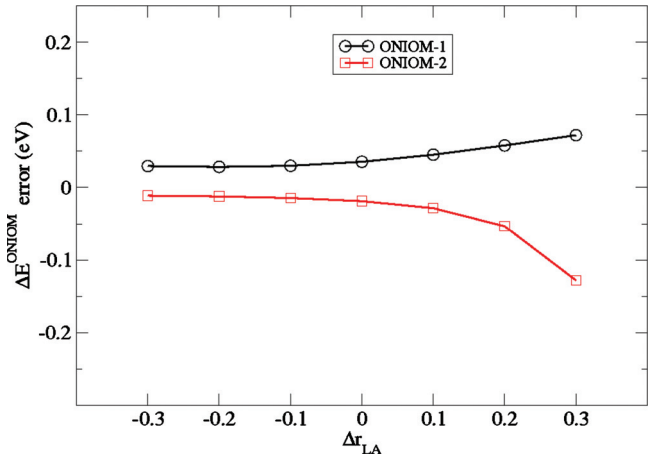


FIG. 22. R-5-aminomethyl-2-oxazolidinone ONIOM transition energy error (eV), Eq. (3), as a function of the r_{LA} shift (Å) from the standard value (see text).

that the ground state definition of r_{LA} is still valid also for excited state calculations and the r_{LA} effect on different transitions is small even when the same model system is used for two molecules with different substituent effects.

E. R-5-aminomethyl-2-oxazolidinone

For R-5-aminomethyl-2-oxazolidinone, the first two electronic transitions can be studied by defining two model systems since they are mainly localized onto different parts of the molecule. In particular, the first transition involves the amino group, so model 1 in Fig. 3(b) can be used, whereas the second transition involves the ring represented by model 2 in Fig. 3(c). r_{LA}=1.105 Å for both models, whereas the original C–C bond is 1.526 Å. The length of the other C–H bonds for the carbon centers where the link atoms are connected to is 1.095–1.096 Å in both models.

E_{GS}^{ONIOM} and E_{exc}^{ONIOM} are rather insensitive to r_{LA} except for drastic elongation and are particularly flat in the ±0.1 Å range (see Fig. 21). This leads to very flat ΔE^{ONIOM} curves in the same region, as reported in Fig. 22. In this case, the ONIOM error remains small for both transitions. Furthermore, Fig. 23 illustrates that both ΔE_{model}^{high} and ΔE_{model}^{low} for both models are only slightly influenced by the variation of r_{LA}. The overall ONIOM insensitivity to such effect is not simply due to error cancellation between the high and low levels also for this case.

Hence, also the results reported in this section seem to point toward the same conclusion, namely, that the ground state definition of r_{LA} is valid for excited state calculations as well, especially when the ONIOM guidelines for the choice of the model system are followed.

IV. DISCUSSION AND CONCLUSION

Some important considerations can be drawn from the different systems we analyzed. Starting from the carboxylic acid, Secs. III A–III C, when the ground state ONIOM partitioning guidelines for the definition of the model system are followed as in model 1, the absolute energies for the ground and the excited states have a similar dependence on r_{LA}. This

suggests that the same guidelines may be also followed for excited state calculations. When the guidelines are not followed as in models 2 and 3, the situation can become more complicated. These models show that the excited state energy can be more sensitive than the ground state, and the choice of the model system is therefore more delicate. In particular, when the link atom is in an area which is affected by the electronic transition even if in its tail, it can significantly influence the ONIOM result. We report a simple analysis based on the natural transition orbitals that can provide some information about the involvement of the link atom in the transition process, and thus on the effectiveness of the chosen partitioning.

This molecule also shows a small dependence of the transition energy on r_{LA} for all the low level methods we compared, in particular, those belonging to the same hierarchy (HF based methods), and even with the more problematic model systems. Additionally, the r_{LA} effect seems to be smaller than the effect of the choice of the low level method, thus TDDFT is confirmed to be preferable over CIS and TDHF, as also concluded in Ref. 15. Considering that the transition energy is an energy difference, this good performance may not only be caused by cancellation of errors between the high and low level terms in the ONIOM extrapolation formula, but also by cancellation of errors between the excited and ground state calculations. For this system (in many cases) the dependence on r_{LA} is small even for the individual ΔE_{model} terms in Eq. (2), especially in the region of ± 0.1 Å around its standard value resulting in an overall small dependence of the integrated ΔE^{ONIOM}. However, other properties depend on the absolute energy (for instance, geometry optimizations) and these results show that, with the proper choice of the model system and DFT as low level, E_{GS}^{ONIOM} and E_{exc}^{ONIOM} do not seem to be particularly sensitive to r_{LA}. On the other hand, HF in the low level shows a large dependence on r_{LA} for both states which makes it less preferable than DFT also from this point of view. CCSD as low level shows, in general, the smallest dependence on r_{LA} for absolute and transition energies, but the computational cost is very high and this method is difficult to apply in production calculations.[15]

The analysis above is strengthened by the results reported in Secs. III D and III E, where three other molecular systems with different chemical groups are investigated. For those molecules, we only consider a partitioning that follows the ground state ONIOM guidelines and TDDFT/L as low level. The ground state r_{LA} definition seems appropriate also for these test cases, and its effect on ONIOM absolute and transition energies in a reasonable range of r_{LA} shifts is negligible.

Based on these results, we propose a few more guidelines for ONIOM excited state calculations. (i) A NTO analysis at the low level of theory on the model system may be useful even when the ground state ONIOM guidelines are followed in order to ensure that no link atom is involved in the transition. (ii) The link atoms should be set far enough apart in order not to interact with each other. (iii) The excited state of interest, in the model system, should be well defined; otherwise, different treatment at different levels of theory may result in unpredictable behaviors.

This paper and our previous work[15] suggest that the same set of guidelines for the definition of the model system in an ONIOM ground state calculation also applies to excited state calculations and the same definition of r_{LA} can be used in both cases. As for conventional excited state methods, ONIOM is more sensitive to the choice of the parameters of the calculation than for the ground state, and we provide additional guidelines to make a sensible choice and check its validity.

[1] M. J. Field, P. A. Bash, and M. Karplus, J. Comput. Chem. **11**, 700 (1990).
[2] U. C. Singh and P. A. Kollman, J. Comput. Chem. **7**, 718 (1986).
[3] A. Warshel and M. Levitt, J. Mol. Biol. **103**, 227 (1976).
[4] S. Dapprich, I. Komáromi, K. S. Byun, K. Morokuma, and M. J. Frisch, J. Mol. Struct.: THEOCHEM **461–462**, 1 (1999).
[5] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, and K. Morokuma, J. Phys. Chem. **100**, 19357 (1996).
[6] S. Humbel, S. Sieber, and K. Morokuma, J. Chem. Phys. **105**, 1959 (1996).
[7] T. Vreven and K. Morokuma, J. Comput. Chem. **21**, 1419 (2000).
[8] T. Vreven and K. Morokuma, *Annual Reports in Computational Chemistry* (Elsevier, Amsterdam, 2006), Vol. 2, Chap. 3, pp. 35–51.
[9] K. Morokuma, D. G. Musaev, T. Vreven, H. Basch, M. Torrent, and D. V. Khoroshun, IBM J. Res. Dev. **45**, 367 (2001).
[10] T. Vreven, K. Morokuma, O. Farkas, H. B. Schlegel, and M. J. Frisch, J. Comput. Chem. **24**, 760 (2003).
[11] T. Vreven, K. S. Byun, I. Komaromi, S. Dapprich, J. A. Montgomery, K. Morokuma, and M. J. Frisch, J. Chem. Theory Comput. **2**, 815 (2006).
[12] M. J. Bearpark, F. Ogliaro, T. Vreven, M. Boggio-Pasqua, M. J. Frisch, S. M. Larkin, M. Morrison, and M. A. Robb, J. Photochem. Photobiol., A **190**, 207 (2007).
[13] F. R. Clemente, T. Vreven, and M. J. Frisch, *Quantum Biochemistry* (Wiley-VCH, Weinheim, 2010), Vol. 1, Chap. 2, pp. 61–83.
[14] T. Vreven and K. Morokuma, J. Chem. Phys. **113**, 2969 (2000).
[15] M. Caricato, T. Vreven, G. W. Trucks, M. J. Frisch, and K. B. Wiberg, J. Chem. Phys. **131**, 134105 (2009).
[16] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem., Quantum Chem. Symp. **18**, 255 (1984).
[17] J. Geertsen, M. Rittby, and R. J. Bartlett, Chem. Phys. Lett. **164**, 57 (1989).
[18] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
[19] S. R. Gwaltney and R. J. Bartlett, Chem. Phys. Lett. **241**, 26 (1995).
[20] S. R. Gwaltney, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **248**, 189 (1996).
[21] R. J. Bartlett and M. Musial, Rev. Mod. Phys. **79**, 291 (2007).
[22] M. Kállay and J. Gauss, J. Chem. Phys. **121**, 9257 (2004).
[23] H. J. Monkhorst, Int. J. Quantum Chem. **Y11**, 421 (1977).
[24] H. Koch and P. Jorgensen, J. Chem. Phys. **93**, 3333 (1990).
[25] P. Slavíček and T. J. Martínez, J. Chem. Phys. **124**, 084107 (2006).
[26] S. Komin and D. Sebastiani, J. Chem. Theory Comput. **5**, 1490 (2009).
[27] E. Derat, J. Bouquant, and S. Humbel, J. Mol. Struct.: THEOCHEM **632**, 61 (2003).
[28] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[29] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[30] P. J. Stephens, F. J. Devlin, C. S. Ashvar, C. F. Chabalowski, and M. J. Frisch, Faraday Discuss. **99**, 103 (1994).
[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision A.03, Gaussian, Inc., Wallingford, CT, 2009.
[32] See supplementary material at http://dx.doi.org/10.1063/1.3474570 for the ground and the transition energy values for all the calculations, Tables I–XIX.
[33] R. L. Martin, J. Chem. Phys. **118**, 4775 (2003).